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VERIFICATION OF A TRANSLATION

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Date: November 27, 2007

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[Title of the Invention] Phosphor, preparing method of phosphor, and plasma display device

[Claims]

[Claim 1] A preparing method of a phosphor, whose emission center is formed by adding at least one of Eu and Mn as an activator and whose host crystal is a composite oxide including at least one element of Ba, Ca, Sr and Mg, comprising:

a reducing atmosphere process for firing a mixed material of the phosphor at least once in a reducing atmosphere, and

an oxidizing atmosphere process for firing in an oxidizing atmosphere after the reducing atmosphere process.

[Claim 2] The preparing method of a phosphor of claim 1, wherein the heating temperature in the oxidizing atmosphere process is 600℃ or more to 1000℃ or less.

[Claim 3] A phosphor obtained in the preparing method of a phosphor of claim 1 or 2, wherein a composition formula of the phosphor is $Ba_{(1-x-y)}Sr_yMgAl_{10}O_{17}:Eu_x$ (where $0.01 \leqq x \leqq 0.20$, $0 \leqq y \leqq 0.30$).

[Claim 4] A plasma display device comprising plural rows of discharge cells of a single color or multiple colors, and phosphor layers of colors corresponding to the discharge cells, the phosphor layers being excited by ultraviolet rays for emitting light,

wherein at least one phosphor layer out of the phosphor layers includes the phosphor of claim 3.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a phosphor and a preparing method of a phosphor, and more particularly the phosphor is preferably usable in an image display device represented by plasma display device, a rare gas discharge lamp, or an illuminating device represented by high load fluorescent lamp.

[0002]

[Background Art]

Recently, among color display devices used in image display of computer or television, a plasma display device is expected as a color display device of large size, thin type, and light weight.

[0003]

The plasma display device is designed to display in full color by adding three primary colors (red, green and blue) by an additive process. For this purpose of full-color display, the plasma display device has phosphor layers for emitting red, green and blue colors. In a discharge cell of the plasma display device, ultraviolet rays of wavelength of 200 nm or less are generated by discharge of rare gas, and the color phosphors are excited by the ultraviolet rays, and visible color lights are generated.

[0004]

The phosphors for emitting colors include, for example, (Y, Gd) BO_3: Eu^{3+}, Y_2O_2S: Eu^{3+} for emitting a red color, (Ba, Sr, Mg) $O \cdot aAl_2O_3$: Mn^{2+}, Zn_2SiO_4: Mn^{2+} for emitting a green color, and $BaMgAl_{10}O_{17}$: Eu^{2+} for emitting a blue color.

[0005]

Among them, in the blue phosphor whose parent body is $BaMgAl_{10}O_{17}$ and called BAM base, Eu of an emission center is required to be activated at divalence to intensity brightness of emission, and it is prepared by firing in a reducing atmosphere (see, for example, non-patent document 1). The reason is that Eu becomes trivalent when this phosphor is fired in oxidizing atmosphere, and cannot correctly replace divalent Ba in the parent body, and hence cannot be an active emission center, and thereby the brightness of emission decreases. Further, the phosphor does not play its role of emitting blue, and a characteristic red color of Eu^{3+} is emitted.

[0006]

The red phosphor, europium activated acid yttrium sulfide (Y_2O_2S: Eu^{3+}), is required to activate Eu at trivalence, and is hence fired in an oxidizing atmosphere and prepared. On the other hand, the phosphor whose host crystal is constituted of an oxide, it is commonly thought that oxygen atoms are removed from the host crystal in firing process, so that oxygen deficiencies are generated. As a method for repairing oxygen deficiencies, an example of firing Y_2O_2S: Eu^{3+} where Eu is activated at trivalence by inert gas containing oxygen is disclosed (see, for example, patent document 1).

[0007]

[Non-patent document]

Phosphor Research Society (ed.): "Phosphor Handbook," p.170, Ohmsha, Ltd.

[Patent document 1]

Japanese Patent Unexamined Publication No. 2000-290649 (pp. 2-3)

[0008]

[Problems to be Solved by the Invention]

However, as compared with a phosphor oxide produced by firing in an oxidizing atmosphere, a phosphor oxide produced by firing in a reducing atmosphere is increased in oxygen deficiencies in the host crystal because oxygen is easily removed from the host crystal in the reducing atmosphere. Yet, if the phosphor oxide to be fired in a reducing atmosphere is fired in an oxidizing atmosphere, it is hard to maintain the original number of valence of an activator.

[0009]

In other words, when ion impact accompanied by discharge or irradiation of ultraviolet rays (wavelength 147 nm) of high energy generated by the plasma display device is applied to the phosphor whose host crystal has many oxygen deficiencies, the phosphor tends to deteriorate with time. This is because bonding between atoms is weak at a place of oxygen deficiencies, and when ultraviolet rays of high energy or ion impact is applied to this place, the crystal structure falls into disorder, and the place tends to be amorphous. The amorphous place means deterioration of the host crystal, and thereby deterioration of brightness with time, color shift by chromaticity variation, or image burn-in may occur in the plasma display device.

[0010]

If a phosphor oxide, which has to be fired in a reducing atmosphere, is fired in an oxidizing atmosphere to repair oxygen deficiencies, for example,

Eu becomes trivalent Eu^{3+} in BAM base phosphor, and conspicuous deterioration of brightness takes place.

[0011]

The invention is devised in the light of such problems, and it is hence an object thereof to present a method of preparing a phosphor capable of repairing oxygen deficiencies without lowering the emission brightness even in a phosphor whose host crystal is an oxide and Eu or Mn of an emission center is required to be activated at divalence, a phosphor of high emission brightness and small deterioration of brightness, and a plasma display device using such phosphor.

[0012]

[Means to Solve the Problems]

The method of preparing a phosphor of the invention is a preparing method of a phosphor, whose emission center is formed by adding at least one of Eu and Mn as an activator and whose host crystal is a composite oxide including at least one element of Ba, Ca, Sr and Mg, including a reducing atmosphere process for firing a mixed material of the phosphor at least once in a reducing atmosphere, and an oxidizing atmosphere process for firing in an oxidizing atmosphere after the reducing atmosphere process. According to this preparing method, oxygen deficiencies of host crystal caused in the reducing atmosphere process are repaired in the oxidizing atmosphere firing, and therefore a phosphor of high emission brightness and small deterioration of brightness is obtained.

[0013]

In the preparing method of a phosphor of the invention, the heating

temperature in the oxidizing atmosphere process is 600℃ or more to 1000℃ or less. According to this preparing method, oxygen deficiencies of host crystal are repaired, and Eu^{3+} hardly appears, so that high brightness without emission of red color is obtained.

[0014]

The phosphor of the invention is composed in a formula of $Ba_{(1-x-y)}Sr_y MgAl_{10}O_{17}$: Eu_x (where $0.01 \leqq x \leqq 0.20$, $0 \leqq y \leqq 0.30$). In such phosphor of aluminate, this preparing method brings about an outstanding effect of repairing oxygen deficiencies of host crystal.

[0015]

The plasma display apparatus of the invention is a plasma display device comprising plural rows of discharge cells of a single color or multiple colors, and phosphor layers of colors corresponding to the discharge cells, the phosphor layers being excited by ultraviolet rays for emitting light, in which at least one phosphor layer out of the phosphor layers includes the above phosphor. According to this plasma display device, emission brightness is high, and the host crystal of the phosphor has only few oxygen deficiencies, and therefore deterioration of emission is suppressed in actual use.

[0016]

[Description of the Preferred Embodiments]

A preferred embodiment of the invention is specifically described below while referring to the accompanying drawings.

[0017]

Fig. 1 is a flowchart of preparing method of a phosphor in a preferred embodiment of the invention, relating to an example of synthesis of Ba Sr

$MgAl_{10}O_{17}$: Eu, which is a kind of phosphor aluminate.

[0018]

In powder weighing process of step 1, the following metal materials--mainly carbonates, oxides and hydroxides--are prepared and weighed. A barium source material includes barium carbonate, barium hydroxide, barium oxide, barium nitrate, and other barium compounds; a strontium source material includes strontium carbonate, strontium hydroxide, strontium nitrate, and other strontium compounds; a magnesium source material includes magnesium carbonate, magnesium hydroxide, magnesium oxide, magnesium nitrate, and other magnesium compounds; an aluminum source material includes aluminum oxide, aluminum hydroxide, aluminum nitrate, and other aluminum compounds; and a europium source material includes europium oxide, europium carbonate, europium hydroxide, europium nitrate, and other europium compounds. These materials are weighed so as to be a certain mole ratio of constitute ions. Although not used in the preferred embodiment of the invention, calcium hydroxide, calcium carbonate, calcium nitrate, or other calcium compound is used as calcium source material.

[0019]

In mixing process of step 2, a flux of crystal growth accelerator is mixed simultaneously in the weighed materials as required, such as aluminum fluoride, barium fluoride, or magnesium fluoride. The mixing means is, for example, a ball mill, which is operated for 1 to 5 hours. The materials may be mixed in wet process by a ball mill, or by coprecipitation or in liquid phase using an alkoxide changed from a metal.

[0020]

In filling process of step 3, the obtained mixture is loaded into a heatproof melting pot, such as an alumina melting pot of high purity.

[0021]

In atmospheric air process of step 4, the loaded mixed powder is heated for 1 to 10 hours in a temperature range of 800℃ to 1500℃ in order to accelerate crystal growth of a host crystal. Step 4 is not essential because it aims to accelerate crystal growth.

[0022]

In reducing atmosphere process of step 5, the mixture is fired in a reducing atmosphere, for example, a mixed atmosphere of hydrogen and nitrogen not containing oxygen, at a temperature enough to form a desired crystal structure. The phosphor aluminate of the preferred embodiment of the invention is fired for 1 to 50 hours in a temperature range of 1100℃ to 1500°℃.

[0023]

In oxidizing atmosphere process of step 6, the mixture is fired again in an oxidizing atmosphere in a temperature range of 600℃ to 1000℃. The phosphor aluminate of the preferred embodiment of the invention is fired for 1 to 50 hours in an oxidizing atmosphere. The oxidizing atmosphere is higher in oxygen partial pressure at least than the reducing atmosphere mentioned above. If the firing temperature is lower than 600℃ in oxidizing atmosphere, the temperature is not high enough for allowing oxygen atoms to enter for repairing oxygen deficiencies, and the oxygen deficiencies are not repaired. If exceeding 1000℃, trivalent Eu ions increase more than

necessary, while divalent Eu ions decrease, and sufficient light emission is not achieved.

[0024]

In pulverizing, dispersing, washing and drying process of step 7, the mixed powder fired in oxidizing atmosphere is sufficiently cooled, and pulverized and dispersed in wet process for about an hour by using a bead mill as dispersing means, and then washed in water. Not limited to beam mill, other dispersing means may be used such as ball mill or jet mill. The powder of pulverized, dispersed and washed phosphor is dehydrated and dried sufficiently, and is passed through a specified sieve, and powder of phosphor is obtained.

[0025]

In the preferred embodiment, the reducing atmosphere process and the subsequent oxidizing atmosphere process are executed only once each, but the reducing atmosphere process for enhancing the brightness of emission by making Eu divalent and the subsequent oxidizing atmosphere process for repairing oxygen deficiencies of host crystal may be repeated plural times. In addition, the atmospheric air process may be executed one or more times before the reducing atmosphere process, or each process may be followed by pulverizing, dispersing and washing process.

[0026]

Fig. 2 is a sectional view of heat treatment apparatus used in the oxidizing atmosphere process in the preferred embodiment of the invention, in which the feed gas adjusted to a specified oxygen concentration is guided into chamber 42 through inlet 41, and oxidizing atmosphere 43 is formed.

In oxidizing atmosphere 43 at ordinary temperature, phosphor powder 45 loaded in alumina melting pot 44 is fired for 1 to 5 hours in a temperature range of 600℃ to 1000℃, and oxygen deficiencies of host crystal are repaired. Heating means 46 is composed of heating coil or infrared lamp. The gas for forming oxidizing atmosphere 43 is properly discharged from outlet 47.

[0027]

The phosphor aluminate $Ba_{(1-x-y)}Sr_yMgAl_{10}O_{17}: Eu_x$ is processed at least in the reducing atmosphere process and subsequent oxidizing atmosphere process, and the characteristics of the obtained phosphors are explained below.

[0028]

(Exemplary embodiment 1)

Powder materials sufficiently dried to a constant weight were prepared: barium carbonate ($BaCO_3$), magnesium carbonate ($MgCO_3$), europium oxide (Eu_2O_3), and aluminum oxide (Al_2O_3). These materials are weighed so as to be a specified mole ratio of constitute ions: Ba: Mg: Eu: Al = 0.99: 1.00: 0.01: 10.00. As crystal growth accelerator, aluminum fluoride was added to the weighed materials, and mixed for 3 hours by a ball mill.

[0029]

Consequently, the mixture was loaded into an alumina melting pot of high purity, and fired for 1 hour at 1200℃ in an atmospheric air. The fired mixed powder was further fired in a reducing atmosphere process for 10 hours at 1200℃ in a reducing atmosphere where the partial pressure ratio is 20% of nitrogen and 80% of hydrogen. In an oxidizing atmosphere, it was further fired for 3 hours at 800℃ in an oxidizing atmosphere where the

partial pressure ratio is 20% of oxygen and 80% of nitrogen.

[0030]

The fired powder was sufficiently cooled, and pulverized and dispersed in wet process for about an hour by using a bead mill, and washed in water. The washed mixed powder of phosphor was dehydrated, dried sufficiently, and passed through a specified sieve, and phosphor powder in composition formula of $Ba_{0.99}MgAl_{10}O_{27}$: $Eu_{0.01}$ was produced.

[0031]

The obtained phosphor powder was exposed to vacuum ultraviolet rays of peak wavelength 146 nm emitted from a vacuum ultraviolet excimer irradiation apparatus (146 nm light irradiation device manufactured by Ushio Inc.), and the brightness per irradiation time was measured by a luminance meter (LS-1110 manufactured by Minolta Camera Co., Ltd.). Herein, as characteristic value of brightness, the relative brightness value defined below is used as an evaluation index. The relative brightness value is the product of relative initial emission intensity of each phosphor multiplied by the brightness maintenance ratio. The relative initial emission intensity is the ratio the initial emission intensity of a material of the exemplary embodiment, assuming the initial emission intensity of the prior art to be 100. The brightness maintenance ratio is the percentage of the brightness of material of exemplary embodiment in 5000 hours divided by the initial emission intensity of material of exemplary embodiment. Or, the relative brightness value is an index of comparing the brightness of phosphor after a specific time between the conventional phosphor and the phosphor of the exemplary embodiment of the invention. Table 1 denotes

composition ratio of materials, process conditions, and relative brightness values.

[0032]

(Exemplary embodiments 2, 3)

Using the same materials as in exemplary embodiment 1, the mole ratio of constitute ions was defined as Ba: Mg: Eu: Al = 0.9: 1.0: 0.1: 10.0 in exemplary embodiment 2, and Ba: Mg: Eu: Al = 0.8: 1.0: 0.2: 10.0 in exemplary embodiment 3. Exemplary embodiments 2 and 3 differ from exemplary embodiment 1 in the following points. In exemplary embodiment 2, the materials were fired in an atmospheric air for 1 hour at 1400℃. and in a reducing atmosphere for 10 hours at 1100℃ at partial pressure ratio of 95% of nitrogen and 5% of hydrogen. In exemplary embodiment 3, the materials were fired in an atmospheric air for 1 hour at 800℃. and in a reducing atmosphere for 10 hours at 1200℃ at partial pressure ratio of 100% of nitrogen. The phosphor powders manufactured in these conditions were evaluated by the relative brightness values same as in exemplary embodiment 1. Table 1 denotes process conditions and relative brightness values.

[0033]

(Exemplary embodiments 4 to 9)

In addition to the materials of exemplary embodiment 1, powder of strontium carbonate ($SrCO_3$) was prepared, and the mole ratio of constitute ions was specified as Ba: Sr: Mg: Eu: Al = 0.89: 0.10: 1.00: 0.01: 10.00 in exemplary embodiment 4, Ba: Sr: Mg: Eu: Al = 0.8: 0.1: 1.0: 0.1: 10.0 in

exemplary embodiment 5, Ba: Sr: Mg: Eu: Al = 0.7: 0.1: 1.0: 0.2: 10.0 in exemplary embodiment 6, Ba: Sr: Mg: Eu: Al = 0.69: 0.30: 1.00: 0.01: 10.00 in exemplary embodiment 7, Ba: Sr: Mg: Eu: Al = 0.6: 0.3: 1.0: 0.1: 10.0 in exemplary embodiment 8, and Ba: Sr: Mg: Eu: Al = 0.5: 0.3: 1.0: 0.2: 10.0 in exemplary embodiment 9. Exemplary embodiments 4 to 9 differ from exemplary embodiment 1 in the following points. In exemplary embodiment 4, not fired in an atmospheric air, the materials were fired in a reducing atmosphere for 10 hours at 1100℃ at partial pressure ratio of 100% of hydrogen. In exemplary embodiment 5, the materials were fired in an atmospheric air for 1 hour at 1300℃. and in a reducing atmosphere for 10 hours at 1200℃ at partial pressure ratio of 99% of nitrogen and 1% of hydrogen. In exemplary embodiment 6, the materials were fired in an atmospheric air for 1 hour at 1400℃. and in a reducing atmosphere for 10 hours at 1400℃ at partial pressure ratio of 90% of nitrogen and 10% of hydrogen. In exemplary embodiment 7, the materials were fired in an atmospheric air for 1 hour at 1300℃. and in a reducing atmosphere for 10 hours at 1300℃ at partial pressure ratio of 98% of nitrogen and 2% of hydrogen. In exemplary embodiment 8, the materials were fired in an atmospheric air for 1 hour at 1000℃. and in a reducing atmosphere for 10 hours at 1300℃ at partial pressure ratio of 90% of nitrogen and 10% of hydrogen. In exemplary embodiment 9, the materials were fired in an atmospheric air for 1 hour at 1200℃. and in a reducing atmosphere for 10 hours at 1300℃ at partial pressure ratio of 50% of nitrogen and 50% of hydrogen. The phosphor powders manufactured in these conditions were evaluated by the relative brightness values same as in exemplary

embodiment 1. Table 1 denotes process conditions and relative brightness values.

[0034]

(Comparative example)

The comparative example is a phosphor of same mole ratio of constitute ions prepared in a conventional method (prior art), and what differs from exemplary embodiment 5 is that it lacks the oxidizing atmosphere process for repairing oxygen deficiencies. The brightness maintenance ratio of this material is 69%, and hence the relative brightness value is 69.

[0035]

[Table 1]

	Mole ratio of constitute ions			Composition formula	Atmospheric air temperature	Reducing atmosphere	Oxidizing atmosphere	Relative brightness
	Ba	Sr	Eu			Temperature, H_2 concentration	Temperature, O_2 concentration	
Exemplary embodiment 1	0.99	0	0.11	$Ba_{0.99}MgAl_{10}O_{17}:Eu_{0.01}$	1200℃	1200℃, 80%		71
Exemplary embodiment 2	0.9	0	0.1	$Ba_{0.9}MgAl_{10}O_{17}:Eu_{0.1}$	1400	1100℃, 5		90
Exemplary embodiment 3	0.8	0	0.2	$Ba_{0.8}MgAl_{10}O_{17}:Eu_{0.2}$	800	1200℃, 0		84
Exemplary embodiment 4	0.89	0.1	0.01	$Ba_{0.89}Sr_{0.1}MgAl_{10}O_{17}:Eu_{0.01}$	—	1100℃, 100		71
Exemplary embodiment 5	0.8	0.1	0.1	$Ba_{0.8}Sr_{0.1}MgAl_{10}O_{17}:Eu_{0.1}$	1300	1200℃, 1	800℃, 20%	88
Exemplary embodiment 6	0.7	0.1	0.2	$Ba_{0.7}Sr_{0.1}MgAl_{10}O_{17}:Eu_{0.2}$	1400	1400℃, 10		90
Exemplary embodiment 7	0.69	0.3	0.01	$Ba_{0.69}Sr_{0.3}MgAl_{10}O_{17}:Eu_{0.01}$	1300	1300℃, 2		74
Exemplary embodiment 8	0.6	0.3	0.1	$Ba_{0.6}Sr_{0.3}MgAl_{10}O_{17}:Eu_{0.1}$	1000	1300℃, 10		84
Exemplary embodiment 9	0.5	0.3	0.2	$Ba_{0.5}Sr_{0.3}MgAl_{10}O_{17}:Eu_{0.2}$	1200	1300℃, 50		71
Comparative example	0.8	0.1	0.1	$Ba_{0.8}Sr_{0.1}MgAl_{10}O_{17}:Eu_{0.1}$	1300	1200℃, 1	—	69

[0036]

As known from Table 1, in phosphor aluminate $Ba_{(1-x-y)}Sr_yMgAl_{10}O_{17}$: Eu_x, in a range of $0.01 \leqq x \leqq 0.20$, $0 \leqq y \leqq 0.30$, the relative brightness is higher than the prior art or comparative example by 11 in average, the emission brightness is enhanced. In exemplary embodiments 1 to 9, the reducing atmosphere firing conditions for preparing samples and the preceding atmospheric air firing conditions are varied, but presence or absence of oxidizing atmosphere firing seems to have a greater effect on the difference in relative brightness rather than the effect on the relative brightness. In particular, between exemplary embodiment 5 and comparative example, which are identical in mole ratio of constitute ions but are different only in presence or absence of oxidizing atmosphere process for repairing oxygen deficiencies, a relative brightness difference of 19 is noted. Effects of oxidizing atmosphere firing are confirmed as explained below.

[0037]

First of all, Eu is widely used as an activator becoming both divalent and trivalent, but in an example of blue phosphor of BAM base, while generating a host crystal of $Ba_{(1-x)}MgAl_{10}O_{17}$ from raw materials, divalent Eu must be displaced with divalent Ba to produce stable emission center Eu^{2+}. For this purpose, in a conventional basic firing method, at high temperature of 1000 to 1500℃, materials are fired for more than 4 hours in a proper reducing atmosphere.

[0038]

Secondly, repairing of oxygen deficiencies of host crystal generated in the reducing atmosphere is confirmed when the firing temperature is more

than 600°C in the case of firing for more than 1 hour in oxidizing atmosphere at partial pressure ratio of 20% of oxygen and 80% of nitrogen. A greater repairing effect was noted at 750℃ or higher temperature. Change of activator Eu from divalent to trivalent due to firing for repairing oxygen deficiencies in oxidizing atmosphere was investigated about BAM: Eu phosphor by reference to occurrence of red emission characteristic of Eu^{3+}, and almost nothing was observed at less than 850℃, but a sudden increase was noted after 1000℃. Thus, change of Eu valence appears only after 1000℃, which may be explained as follows. That is, to displace divalent Ba in BAM until the stable divalent Eu becomes trivalent, from the viewpoint of charge compensation, an empty lattice must be produced by surrounding Eu in the host crystal, and it is accompanied by move of atoms in the host crystal, and this reaction requires a high temperature exceeding 1000℃ corresponding to crystal growth. Accordingly, when repairing oxygen deficiencies in host crystal by oxidizing atmosphere firing, when the firing temperature is 600℃ or more to 1000℃ or less, more preferably in a range of 750℃ to 850℃, the stable divalent Eu in the BAM: Eu produced in reducing atmosphere is not changed to trivalent, and oxygen deficiencies can be repaired, and a stable phosphor oxide is obtained.

[0039]

Sr is not always required in composition of the phosphor, but when Sr is included, a part of Ba^{2+} replaces Sr^{2+} of smaller ionic radius, and the lattice constant of crystal structure is reduced somewhat, and the luminescent color of blue phosphor may be brought to a more desirable color.

[0040]

Fig. 3 is an essential perspective view of plasma display device of the preferred embodiment of the invention. Front panel PA1 includes transparent and insulating front substrate 11, on which display electrode 15 having scanning electrode 12a and sustain electrode 12b, and dielectric layer 13 are formed to cover them, and protective layer 14 is formed on the dielectric layer 13.

[0041]

A specified number of display electrodes 15 are formed on front substrate 11 at specified pitches. Dielectric layer 13 is required to cover display electrodes 15 completely after display electrodes 15 are formed, and hence it is generally formed by printing and firing low melting glass. Glass paste material is, for example, low melting glass paste having glass composition of (PbO-SiO_2-B_2O_3-ZnO-BaO) system including lead oxide (PbO), silicon oxide (SiO_2), boron oxide (B_2O_3), zinc oxide (ZnO), and barium oxide (BaO). By using this glass paste, for example, by repeating screen printing and firing, dielectric layer 13 of desired film thickness may be obtained easily. The film thickness may be properly determined depending on the thickness of display electrode 15 or target electrostatic capacity. In the preferred embodiment of the invention, the film thickness of the dielectric layer 13 is about 40 μm. The glass paste may be mainly composed of at least one of lead oxide (PbO), bismuth oxide (Bi_2O_3), and phosphorus oxide (PO_4).

[0042]

Protective layer 14 is intended to prevent dielectric layer 13 from being sputtered by plasma discharge, and its material is required to be excellent in sputtering resistance. Hence, magnesium oxide (MgO) is used

preferably.

[0043]

On the other hand, similarly on a transparent and insulating rear electrode 16, data electrodes 17 for writing image data are formed in a direction orthogonal to display electrodes 15 on front panel PA1. To cover the data electrodes 17, insulator layer 18 is formed on the face of rear electrode 16, and parallel to data electrodes 17, barrier walls 19 are formed nearly in the center of data electrodes 17. In a region surrounded by barrier walls 19, phosphor layer 20 is formed, and rear panel PA2 is composed. Phosphor layer 20 has phosphors for emitting red light, green light, and blue light disposed adjacently, and pixels are formed of these elements.

[0044]

Data electrodes 17 are formed in single layer structure of silver, aluminum or copper of low resistance, two-layer structure of chromium and copper, three-layer structure of chromium, copper and chromium, or other laminated structure, by printing and firing method, sputtering, or other thin film forming technology. Insulating layer 18 may be formed in same material and same film forming method as dielectric layer 13. Further, glass paste mainly composed of at least one of lead oxide (PbO), bismuth oxide (Bi_2O_3), and phosphorus oxide (PO_4) may be used. The phosphors manufactured in this manner and emitting red light, green light, and blue light are applied to the region surrounded by barrier walls 19 by, for example, ink jet process, and phosphor layer 20 is formed.

[0045]

When front panel PA1 and rear panel PA2 are placed face to face,

discharge space 30 is formed, which is enclosed by barrier walls 19, protective layer 14 on front substrate 11, and phosphor layer 20 on rear substrate 16. Discharge space 30 is filled with mixed gas of Ne and Xe at a pressure of about 66.5 kPa, and an alternating-current voltage of about tens to hundreds of kHz is applied between scanning electrode 12a and sustain electrode 12b to induce discharge, and phosphor layer 20 is excited by ultraviolet rays generated when excited Xe atoms return to the base state. By this excitation, phosphor layer 20 emits red light, green light or blue light depending on the applied material, and by selecting the emitting pixel and color by data electrodes 17, a desired color can be emitted from a specific pixel, and color images can be displayed.

[0046]

Fig. 4 shows the changing rate of brightness of the phosphor used in the plasma display device. A pulse voltage of amplitude of 180 V and frequency 15 kHz is applied between display electrodes 15, and the phosphor of exemplary embodiment 5 manufactured in the preferred embodiment of the invention, and the phosphor of comparative example manufactured in the conventional method are compared in time-course changes of emission brightness. Emission brightness in initial phase of lighting is supposed to be 100%, and the emission brightness in later phase of lighting is divided by the emission brightness in initial phase of lighting, and brightness changing rate is calculated. The brightness changing rate after lighting for 5000 hours is lowered to 72% in the phosphor of the conventional manufacturing method, and is maintained at 84% in the phosphor of the manufacturing method of the invention, and an improvement effect of 12% is obtained from

the viewpoint of brightness change, and brightness deterioration is suppressed. The phosphor manufactured in the method of the preferred embodiment of the invention is first fired in reducing atmosphere and then fired in oxidizing atmosphere, and the crystal structure of the phosphor contains few oxygen deficiencies, and amorphous structure is decreased. As a result, crystal structure hardly deteriorates in spite of ultraviolet irradiation or ion impact, and brightness deterioration is suppressed.

[0047]

In the preferred embodiment, Eu^{2+} is used as activator in BAM base, but $CaMgSi_2O_6$: Eu using other Eu^{2+} activator, or green phosphor (Ba, Sr, Mg) $O \cdot aAl_2O_3$: Mn using oxide having Mn^{2+} as activator as host crystal is also found to be high in emission brightness by oxidizing atmosphere firing, and is effective in suppression of brightness deterioration.

[0048]

[Advantage of the Invention]

The method of preparing a phosphor of the invention is a preparing method of a phosphor, whose emission center is formed by adding at least one of Eu and Mn as an activator and whose host crystal is a composite oxide including at least one element of Ba, Ca, Sr and Mg, including a reducing atmosphere process for firing a mixed material of the phosphor at least once in a reducing atmosphere, and an oxidizing atmosphere process for firing in an oxidizing atmosphere after the reducing atmosphere process. According to this preparing method, even in the phosphor whose emission center is formed by adding at least one of Eu and Mn as an activator, oxygen deficiencies can be repaired without lowering the emission brightness, and

such manufacturing method of a phosphor is presented, together with the phosphor of high emission brightness and small brightness deterioration, and the plasma display device using the same.

[Brief Description of the Drawings]

Fig. 1 is a flowchart of preparing method of a phosphor according to a preferred embodiment of the invention.

Fig. 2 is a sectional view of heat treatment apparatus used in oxidizing atmosphere process in the preferred embodiment of the invention.

Fig. 3 is an essential perspective view of plasma display device in the preferred embodiment of the invention.

Fig. 4 is a graph of brightness changing rate of phosphors used in the plasma display device in the preferred embodiment of the invention.

[Description of the Reference Numerals and Signs]

11 Front substrate

12a Scanning electrode

12b Sustain electrode

13 Dielectric layer

14 Protective layer

15 Display electrode

16 Rear substrate

17 Data electrode

18 Insulator layer

19 Barrier wall

20 Phosphor layer

30 Discharge space

41	Inlet
42	Chamber
43	Oxidizing atmosphere
44	Alumina melting pot
45	Phosphor powder
46	Heating means
47	Outlet
PA1	Front panel
PA2	Rear panel